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The objective of the work was to extend our basic knowledge of nitration, the fundamental reaction producing high energy nitrogen compounds. Studies included exploration of new areas of aliphatic electrophilic nitration, improved preparative routes to known high energy compounds such as TNT and TNB (1,3,5-trinitrobenzene) and safe new methods to prepare O- and nitrogen compounds.

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HIGH ENERGY NITROGEN COMPOUNDS

The objective of the work was to extend our basic knowledge of nitration, the fundamental reaction producing high energy nitrogen compounds, Studies included exploration of new areas of aliphatic electrophilic nitration, improved preparative routes to known high energy compounds such as TNT and TNB (1,3,5-trinitrobenzene) and safe new methods to prepare O- and nitrogen compounds.

All objectives of the research project were met. A new, efficient method for the trinitration of benzene to trinitrobenzene (TNB) was worked out using nitric-fluorosulfuric acid.

Mechanistic studies of the nitration of aromatics (both electrophilic, nucleophilic and free radical) were continued. The independence of substrate from regioselectivity in the nitration of reactive aromatics (toluene, anisole, o-xylene) was firmly established, clearly indicating the involvement of two separate reaction steps. No simple, linear relationship can thus exist. Free radical nitration and nitrolysis of aromatics, such as diarylhalonium ions, was also studied.

The use of pyridinium polyhydrogen fluoride as reaction medium for nitronium salt nitrations was found to be highly effective. This solvent has no oxidizing ability, is an excellent solvent for both organic substrates and nitronium salts alike, and thus shows promise in minimizing oxidative side reactions.

The nitration of aliphatic and cycloaliphatic hyd[illegible]ons was continued under electrophilic conditions. Further preparative [illegible] for nitroaliphatic compounds, including nitroalkanes, nitroalkenes and nitr[illegible]amantane were developed. Work continued on the possible synthesis of tetranitroadamantane and hexanitrobenzene.

The following list of publications refers to published papers containing details of the work.

BIBLIOGRAPHY (PUBLISHED PAPERS) DAHC04-75-6-0110

G. A. Olah, A. Germain, H. C. Lin and D. A. Forsyth — Electrophilic Reactions at Single Bonds. XVIII. Indication of Protosolvated de facto Substituting Agents in the Reactions of Alkanes with Acetylium and Nitronium Ions in Superacidic Media. J. Am. Chem. Soc. 97, 2928 (1975).

G. A. Olah — Electrophilic Nitration (invited paper presented at the Symposium on Industrial and Laboratory Nitration of the American Chemical Society, Philadelphia Meeting, April 1975). ACS Symposium Monograph Series, Vol. 22, eds. L. F. Albright and C. Hanson, pp. 1-47 (1976).

G. A. Olah, H. C. Lin and A. Serianz — Synthetic Methods & Reactions. XVI. The Nitramine Rearrangement of N-Nitrodimethylanilines. A Novel Route for the Conversion of 3-Nitro-o-xylene. Synthesis 42 (1976).

G. A. Olah, H. C. Lin, J. A. Olah and S. C. Narang — Variation in the Isomer Distribution in the Electrophilic Nitration of Toluene, Anisole and ortho-Xylene. The Independence of High Regioselectivity from the Reactivity of the Reagent. Proc. Natl. Acad. Sci. (in press).

G. A. Olah, T. Sakakibara and G. Asensio — Improved Preparation, Carbon-13 NMR Spectroscopic Structural Study and Nucleophilic Nitrolysis of Diarylhalonium Ions. J. Org. Chem (in press).